

## Adiabatic Jacobi corrections on the vibrational energy levels of $\text{H}_2^+$ isotopologues

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The effect of an adiabatic approximation, named adiabatic Jacobi correction (AJC) and introduced in *J. Chem. Phys.* **126**, 024102 (2007), was investigated on the complete set of vibrational levels of  $\text{H}_2^+$  and its isotopologues, most importantly on the highest-lying vibrational states of  $\text{HD}^+$ . In order to perform clamped nuclei calculations employing finite nuclear masses a constrained Hamiltonian has been derived utilizing interparticle coordinates. The Born–Oppenheimer (BO) potential, the adiabatic potential obtained after taking into account the traditional diagonal Born–Oppenheimer correction (DBOC), as well as the AJC-corrected potential have been determined by an accurate fitting to computed energy values. These potentials were included in one-dimensional variational computations and yielded the complete set of energy levels for  $\text{H}_2^+$ ,  $\text{D}_2^+$ , and  $\text{HD}^+$ . A detailed investigation of the potential and the complete set of vibrational energy levels show the merits and the deficiencies of the BO, DBOC, and AJC treatments. In particular, it is shown that the AJC corrections are systematically smaller and have a different distance dependence than the DBOC corrections. For a large part of the spectrum of  $\text{H}_2^+$  and its isotopologues the adiabatic correction to the vibrational energy levels is smaller than the nonadiabatic correction, the adiabatic DBOC correction has the highest overall accuracy for the prediction of vibrational energy levels, it is surpassed by the AJC correction only for the highest energy levels of  $\text{HD}^+$ , and thus the use of the AJC correction is clearly the best choice only for states close to the dissociation limit of nonsymmetric isotopologues. © 2009 American Institute of Physics. [DOI: 10.1063/1.3097327]

### I. INTRODUCTION

The description whereby electrons move in the (mean) external field provided by clamped nuclei [the Born–Oppenheimer (BO) approximation<sup>1,2</sup>] underpins most of the quantum chemical models used presently for the investigation of the structure and spectroscopy of many-electron molecular systems. Despite considerable successes achieved by approaches based on the BO approximation, for accurate high-resolution prediction of the rovibrational spectrum of water, see, e.g., Ref. 3, there have always been investigations trying to go beyond the BO approach even where it does not “break down.” Many of these studies utilized the simple hydrogen molecular cation ( $\text{H}_2^+$ ) and its isotopologues as a test system. In the early days these investigations were driven mostly by the curiosity of theorists, while during the last two decades further impetus was provided by experiments, for example, those trying to probe the proton-electron and deuteron-electron mass ratios<sup>4,5</sup> through ultrahigh-precision molecular spectroscopy. The nonadiabatic energy levels as well as the adiabatic potentials and the related rotational-vibrational energy levels of the  $\text{H}_2^+$  system, including those of nonsymmetric isotopologues, in particular,  $\text{HD}^+$ , have been the subject of a large number of clamped nuclei,<sup>6–11</sup> three-body,<sup>12–16</sup> and other theoretical<sup>5,17–37</sup> and

experimental<sup>38–47</sup> studies of general interest. Many of these investigations were summarized in insightful reviews.<sup>43,48–51</sup>

Some of the interests in and the difficulties of the experimental studies on  $\text{H}_2^+$  isotopologues are as follows: (a)  $\text{H}_2^+$  and  $\text{D}_2^+$  do not possess permanent electric dipole moments and there are no observable rotational or vibrational transitions in the infrared region of the electromagnetic spectrum leaving related studies to the vacuum ultraviolet region, hindered by diminishing Franck–Condon factors; (b) the hydrogen molecular cation and its deuterated isotopologues play an outstanding role in astrophysics and astrochemistry through their involvement in ion-molecule reactions; and (c) although  $\text{H}_2^+$  is thermodynamically fairly stable, it is very reactive, so it is very hard to keep it separated from the parent  $\text{H}_2$  molecule from which it is usually generated.

As to theory, it is hard to find a better molecule allowing for tests of elementary aspects of quantum chemistry. The notable features of this species include the following: (a) it has only three particles and contains no electron-electron repulsion; (b) for the homonuclear case (e.g.,  $\text{H}_2^+$ ), the two lowest electronic states arising within the BO approximation have different symmetries, thus they cannot interact, leaving a single, extremely well separated ground electronic state for studies of the characteristics of the BO approximation under the best scenario; (c) for the heteronuclear case (e.g.,  $\text{HD}^+$ ), there are still only two lowest interacting electronic states but in the adiabatic (finite mass) cases they can strongly interact

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and thus are ideal to study BO breakdown effects. In fact, the motivation behind some of the theoretical studies was to investigate the “possibility of constructing a single internuclear potential that would include, at least partly, nonadiabatic corrections and thus would yield (accurate) vibrational and rotational eigenvalues.”<sup>23</sup> Thus, besides nonadiabatic computations<sup>52,53,14,19,15</sup> of molecular energies of  $\text{H}_2^+$  and its isotopologues allowed by the simplicity of this system, there have been computations of different adiabatic energy corrections to the simple BO potential.<sup>17,21,25–27,10,29</sup> Overall, it is fair to say that we understand the structure and dynamics of the  $\text{H}_2^+$  ion and its isotopologues better than those of any other chemical species.

In the case of  $\text{HD}^+$ , perhaps the most interesting isotopologue of  $\text{H}_2^+$ , symmetry of the molecular Hamiltonian under exchange of the nuclei is broken due to the mass difference between the proton and the deuteron. Discrimination between the two related dissociation limits,  $\text{H}^+\text{+D}$  and  $\text{D}^+\text{+H}$ , cannot be achieved within the BO approximation. This symmetry breaking couples the nuclear and electronic degrees of freedom and gives rise to an interaction between, for example, the first two BO electronic states at intermediate distances and a splitting of about  $29\text{ cm}^{-1}$  at infinite separation. Of course, the small energy separation of the two lowest states affects the vibrational energies of both states close to the dissociation limits. One must go beyond the BO picture and employ the so-called adiabatic approximations to account for these effects in at least a semiquantitative way. Another consequence of the interaction of the two states is that a permanent dipole is formed both in the ground and the excited electronic states, contributing to a measurable IR spectrum for  $\text{HD}^+$ . In turn this provides a wealth of experimental results for comparison with their first-principles counterparts.

In a recent publication,<sup>35</sup> hereafter referred to as Part 1, two of the authors of this article investigated an adiabatic approximation applied to  $\text{H}_2^+$  and its isotopologues, whereby the full molecular Coulombic Hamiltonian of the nuclei and the electrons was reduced to an adiabatic Hamiltonian by fixing the internuclear coordinate and introducing no other approximations. The resulting Hamiltonian with proper nuclear and electronic masses can be solved, at a chosen internuclear separation, variationally to any desired accuracy yielding total energies and corresponding wave functions. The so-called adiabatic Jacobi energy corrections were defined as the difference in the energies of molecular systems obtained with finite and infinite nuclear masses. If the constrained geometric parameters present in the Hamiltonian correspond to those fixing the spatial arrangement of the nuclei, one recovers the traditional notion of a potential energy surface (PES). If nuclear masses are chosen to be infinite, one obtains the BO-PES; while using finite masses one obtains an adiabatic PES.

Of course, adiabatic Jacobi corrections (AJCs) are not the only adiabatic corrections to the clamped-nuclei (BO) PES investigated in the literature. In the development of adiabatic treatments the guiding principle is that the Hamiltonian so derived should contain as much of the original full Hamiltonian as possible and desirable. In case the adiabatic

treatment is aimed at developing a theory of electronic structure, it is highly desirable if the adiabatic Hamiltonian retained the useful and appealing concept of an internuclear potential energy curve or surface. This can be achieved in several ways. For example, Pack and co-workers<sup>21,25,27</sup> investigated the so-called “standard adiabatic” (SA), the “first-order adiabatic,” the “improved adiabatic,” and the “best adiabatic” approximations for the vibrational-rotational states of  $\text{HD}^+$ . Following Greene,<sup>24</sup> Macek and Jerjian<sup>26</sup> studied the “hyperspherical adiabatic” approximation. Furthermore, Moss<sup>10</sup> introduced the notion of a “partitioned adiabatic” correction.

We will discuss only the SA approximation, as it is exactly the same as the diagonal Born–Oppenheimer correction (DBOC), which is the modern and widely accepted name of this adiabatic approximation. The DBOC correction has been advocated<sup>30,54–58</sup> to move simply beyond the BO approximation. The DBOC energy correction is defined by means of the integral

$$E^{\text{DBOC}}(\mathbf{X}) = -\frac{1}{2} \sum_{a=1}^A \langle \psi(\mathbf{x}, \mathbf{X}) | \frac{\nabla^2(\mathbf{X}_a)}{M_a} | \psi(\mathbf{x}, \mathbf{X}) \rangle_{\mathbf{x}}, \quad (1)$$

where  $\psi(\mathbf{x}, \mathbf{X})$  is the electronic wave function calculated in the clamped nucleus approximation, the electronic and the  $A$  sets of nuclear coordinates are designated by  $\mathbf{x}$  and  $\mathbf{X}$ , respectively. This is the leading term in the corrections arising in the Born–Huang<sup>2</sup> approach to the separation of electronic and nuclear motion. For an isolated atom,  $E^{\text{DBOC}}$  is independent of the nuclear coordinates and reduces to a number. As written by Moss,<sup>10</sup> the DBOC “can be thought of as due to the response of the nuclei to the instantaneous position of the electron so that the uniformity of motion of the molecular center of mass is maintained.” As to nonsymmetric isotopologues of  $\text{H}_2^+$ , due to the neglect of off-diagonal terms in the Hamiltonian, the DBOC correction is unable to discriminate between the  $\text{H}^+\text{+D}$  and  $\text{H+D}^+$  asymptotes; therefore, there is room for better adiabatic approximations. The AJC correction seemed to be one interesting candidate to move simply beyond the DBOC correction.

The most notable problem of Part 1,<sup>35</sup> which prompted this follow-up study, resulted from the use of the orthogonal Jacobi coordinates and manifested in the extraordinarily slow convergence with respect to basis size during the AJC energy calculations, especially at large internuclear separations. This convergence problem can be avoided by choosing a more suitable coordinate system, which, at the same time, facilitates the use of compact basis sets at all internuclear separations.<sup>59</sup> The nonorthogonal coordinate system comprised of the three particle-particle distances is such a coordinate system. This coordinate system is particularly useful as it allows constraining the internuclear distance and at the same time the use of a highly efficient basis. In order to employ this coordinate system, (a) the constrained Hamiltonian must be developed, (b) a suitable basis must be found, and (c) the high-precision, preferably analytic, computation of the required matrix elements must be worked out.

This study is aimed at determining the AJC contributions to all the vibrational energy levels of the isotopologues of

H<sub>2</sub><sup>+</sup>. This requires the computation of the AJC-corrected BO potential followed by a simple one-dimensional nuclear motion computation. In some cases the computed vibrational energy levels can be compared to those derived from experiments<sup>38–47</sup> and in all cases they can be compared to fully nonadiabatic computational results.<sup>16,32</sup> The results obtained also offer some insight into the unusual world of vibrational levels near dissociation limits. Finally, this investigation should be helpful for our planned studies of the vibrational states of H<sub>3</sub><sup>+</sup> and its isotopologues close to their first dissociation asymptotes.

## II. THEORY

Let  $r_{12}$ ,  $r_{13}$ , and  $r_{23}$  denote the distances between the three particles of a three-body system. As to adiabatic approximations, this choice of the internal coordinates offers the same advantage as the Jacobi coordinates, namely, that it is straightforward to fix one of the internuclear distances, for example, the  $r_{12}$  coordinate characterizing the internuclear separation in the case of H<sub>2</sub><sup>+</sup>-like systems (two nuclei at po-

sitions 1 and 2 and an electron at position 3). The three Euler angles  $\phi$ ,  $\theta$ , and  $\psi$  have been chosen to describe the orientation of the space-fixed versus body-fixed axes. The origin of the rotating frame corresponds to the center of mass of the first and the second particles. These two particles lie along the  $z'$  axis of the rotating frame, while the plane generated by the three masses was chosen to be the  $x'z'$  plane. The integration volume element over these coordinates is  $r_{12}r_{13}r_{23} \sin \theta dr_{12}dr_{13}dr_{23}d\phi d\theta d\psi$ . In the rotationless case of  $J=0$  considered here, where  $J$  is the usual rotational quantum number, the resulting Hamiltonian can be expressed in terms of the three internal coordinates. Of course, states obtained with this Hamiltonian will exhibit  $\Sigma$  symmetry.

### A. The $J=0$ Hamiltonians

For the sake of simplicity atomic units will be used throughout the derivation. In this, after separating off the center-of-mass and rotational motions the three-dimensional Hamiltonian of the three-particle system given in the nonorthogonal coordinate system comprised of the three interparticle distances takes the following well-known form:<sup>12</sup>

$$\begin{aligned} \hat{H}^{\text{full}}(r_{12}, r_{13}, r_{23}) = & \hat{T}^{\text{full}} + \hat{V} = -\frac{1}{2} \left( \frac{1}{m_1} + \frac{1}{m_2} \right) \left( \frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}} \frac{\partial}{\partial r_{12}} \right) - \frac{1}{2} \left( \frac{1}{m_1} + \frac{1}{m_3} \right) \left( \frac{\partial^2}{\partial r_{13}^2} + \frac{2}{r_{13}} \frac{\partial}{\partial r_{13}} \right) - \frac{1}{2} \left( \frac{1}{m_2} + \frac{1}{m_3} \right) \left( \frac{\partial^2}{\partial r_{23}^2} \right. \\ & \left. + \frac{2}{r_{23}} \frac{\partial}{\partial r_{23}} \right) - \frac{1}{m_1} \frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{2r_{12}r_{13}} \frac{\partial^2}{\partial r_{12} \partial r_{13}} - \frac{1}{m_2} \frac{r_{12}^2 + r_{23}^2 - r_{13}^2}{2r_{12}r_{23}} \frac{\partial^2}{\partial r_{12} \partial r_{23}} - \frac{1}{m_3} \frac{r_{13}^2 + r_{23}^2 - r_{12}^2}{2r_{13}r_{23}} \frac{\partial^2}{\partial r_{13} \partial r_{23}} \\ & + \hat{V}(r_{12}, r_{13}, r_{23}), \end{aligned} \quad (2)$$

where the potential is defined as

$$\hat{V}(r_{12}, r_{13}, r_{23}) = \frac{1}{r_{12}} - \frac{1}{r_{13}} - \frac{1}{r_{23}}. \quad (3)$$

Due to the nonorthogonal nature of the coordinates employed, three cross terms appear in this Hamiltonian making it nonseparable in these coordinates.

If two of the masses, for example,  $m_1$  and  $m_2$ , corresponding to the choice of  $r_{12}$  as the internuclear distance tend to infinity, the Hamiltonian becomes

$$\begin{aligned} \hat{H}^{\text{BO}}(r_{13}, r_{23}; r_{12}) = & \hat{T}^{\text{BO}}(r_{13}, r_{23}; r_{12}) + \hat{V}(r_{13}, r_{23}; r_{12}) \\ = & -\frac{1}{2m_3} \left( \frac{\partial^2}{\partial r_{13}^2} + \frac{2}{r_{13}} \frac{\partial}{\partial r_{13}} \right) \\ & - \frac{1}{2m_3} \left( \frac{\partial^2}{\partial r_{23}^2} + \frac{2}{r_{23}} \frac{\partial}{\partial r_{23}} \right) \\ & - \frac{1}{m_3} \frac{r_{13}^2 + r_{23}^2 - r_{12}^2}{2r_{13}r_{23}} \frac{\partial^2}{\partial r_{13} \partial r_{23}} \\ & + \hat{V}(r_{13}, r_{23}; r_{12}). \end{aligned} \quad (4)$$

If  $r_{12}$  is treated as a fixed parameter, this Hamiltonian corresponds to the clamped nuclei approximation, which can also be called the BO approximation leading to the BO PES. Hereby one neglects all coupling of nuclear and electronic motions as terms involving inverse nuclear masses are basically dropped.

Now, consider again the Hamiltonian of the full three-body problem with finite masses, Eq. (2). This time the one and only simplification to be introduced is the adiabatic separation of the  $r_{12}$  coordinate, resulting in the AJC approximation and simplifying the dynamics of the problem from a three-dimensional to a two-dimensional case. Consequently,  $r_{12}$  becomes a constant, and in contrast to the clamped nuclei approximation, the two nuclei now have finite masses. To proceed, one must develop the corresponding constrained Hamiltonian. Since this is done in the standard way,<sup>60,61</sup> only the main steps of the derivation are sketched here.

The correct form of the constrained Hamiltonian must be derived from the classical description of the three-body problem. The Lagrangian of a mechanical system comprising  $N$  particles can be given in general by the equation

TABLE I. The first- and second-derivative terms of the constrained  $J=0$  kinetic energy operator in interparticle coordinates keeping  $r_{12}$  as a fixed parameter.

$\frac{\partial^2}{\partial r_{13}^2}$	$-\frac{1}{2}\left(\frac{1}{m_3} + \frac{1}{m_1 + m_2}\right) + \frac{m_2}{8m_1(m_1 + m_2)} \frac{(r_{12} - r_{13} - r_{23})(r_{12} + r_{13} - r_{23})(r_{12} - r_{13} + r_{23})(r_{12} + r_{13} + r_{23})}{r_{12}^2 r_{13}^2}$
$\frac{\partial}{\partial r_{13}}$	$-\frac{1}{2}\left(\frac{1}{m_3} + \frac{1}{m_1 + m_2}\right) \frac{2}{r_{13}} + \frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{2(m_1 + m_2)r_{12}^2 r_{13}} - \frac{m_2(r_{12}^4 - 3r_{13}^4 + 2r_{13}^2 r_{23}^2 + r_{23}^4 + 2r_{12}^2(r_{13} - r_{23})(r_{13} + r_{23}))}{8m_1(m_1 + m_2)r_{12}^2 r_{13}^3}$
$\frac{\partial^2}{\partial r_{23}^2}$	$-\frac{1}{2}\left(\frac{1}{m_3} + \frac{1}{m_1 + m_2}\right) + \frac{m_1}{8m_2(m_1 + m_2)} \frac{(r_{12} - r_{13} - r_{23})(r_{12} + r_{13} - r_{23})(r_{12} - r_{13} + r_{23})(r_{12} + r_{13} + r_{23})}{r_{12}^2 r_{23}^2}$
$\frac{\partial}{\partial r_{23}}$	$-\frac{1}{2}\left(\frac{1}{m_3} + \frac{1}{m_1 + m_2}\right) \frac{2}{r_{23}} - \frac{m_1(r_{12}^2 - r_{13}^2)^2 + 2((m_1 - 2m_2)r_{12}^2 + (m_1 + 2m_2)r_{13}^2)r_{23}^2 - (3m_1 + 4m_2)r_{23}^4}{8m_2(m_1 + m_2)r_{12}^2 r_{23}^3}$
$\frac{\partial^2}{\partial r_{13} \partial r_{23}}$	$-\frac{1}{2}\left(\frac{1}{m_3} + \frac{1}{m_1 + m_2}\right) \frac{r_{13}^2 + r_{23}^2 - r_{12}^2}{r_{13} r_{23}} - \frac{1}{4(m_1 + m_2)} \frac{(r_{12} - r_{13} - r_{23})(r_{12} + r_{13} - r_{23})(r_{12} - r_{13} + r_{23})(r_{12} + r_{13} + r_{23})}{r_{12}^2 r_{13} r_{23}}$

$$L = \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} g_{ij} \dot{q}_i \dot{q}_j - V, \quad (5)$$

where

$$g_{ij} = \sum_{k=1}^N \sum_{l=1}^3 m_k \frac{\partial x_{kl}}{\partial q_i} \frac{\partial x_{kl}}{\partial q_j}. \quad (6)$$

In Eq. (6)  $m_k$  is the mass of the  $k$ th particle, while  $x_{kl}$  refers to the  $l$ th Cartesian coordinate ( $l=1, 2, 3$ ) of the  $k$ th particle and  $q_i$  corresponds to the  $i$ th generalized coordinate. The corresponding classical Hamiltonian can be obtained by employing the

$$H = \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} G_{ij} p_i p_j + V \quad (7)$$

formula, where

$$G_{ij} = (\mathbf{g}^{-1})_{ij}. \quad (8)$$

In order to fix the generalized coordinate  $q_i$ , the  $i$ th row and the  $i$ th column of  $\mathbf{g}$  must be erased. Thus one obtains a constrained  $\mathbf{g}$  matrix, which results in a constrained  $\mathbf{G}$  matrix after inversion. The  $G_{ij}$  matrix elements generate the constrained classical Hamiltonian, which can be transformed into a constrained quantum mechanical Hamiltonian. Note that although the deletions can be carried out in the  $\mathbf{G}$  matrix as well, the physical meaning radically differs from the case where they are performed in  $\mathbf{g}$ . The  $\mathbf{G}$ -based approach corresponds to fixing the  $i$ th canonical momentum instead of the  $i$ th generalized coordinate and may lead to strange situations when the computed adiabatic correction depends on the chosen set of generalized coordinates.

In order to avoid the completely continuous part of the spectrum of the three-body Coulomb Hamiltonian, the translational motion is separated by using nuclear center-of-mass coordinates. Thus, a Lagrangian expressed in terms of the three internal coordinates and the three Eulerian angles is obtained. After fixing  $r_{12}$ , the constrained Lagrangian can be transformed to a constrained classical Hamiltonian. At this stage the Podolsky transformation<sup>62</sup> can be invoked in order

to obtain the constrained Hamiltonian operator. Since we are dealing with the  $J=0$  case, the resulting Hamiltonian has the form

$$\hat{H}^{\text{AJC}}(r_{13}, r_{23}; r_{12}) = \hat{T}^{\text{AJC}}(r_{13}, r_{23}; r_{12}) + \hat{V}(r_{13}, r_{23}; r_{12}), \quad (9)$$

where the terms appearing in the  $\hat{T}^{\text{AJC}}$  kinetic energy operator are given in Table I.

In the case of  $\text{H}_2^+$  and its isotopologues, three unit charges are present in  $\hat{V}$  with the particle of mass  $m_3$  having the negative unit charge, and the other two particles with masses  $m_1$  and  $m_2$  are chosen to have positive unit charges. It is straightforward to check that the  $\hat{H}^{\text{AJC}}$  Hamiltonian will result in the BO Hamiltonian  $\hat{H}^{\text{BO}}$  of Eq. (4) if the masses  $m_1$  and  $m_2$  are chosen to be infinite.

Finally, let us consider another reduced-dimensional model developed by simultaneously constraining the  $r_{12}$ ,  $\phi$ , and  $\theta$  coordinates. The two angles describe the overall rotation of the two nuclei. While  $r_{12}$  is treated as a fixed parameter, the values of  $\phi$  and  $\theta$  have been set to 0 throughout the derivation. This choice of the two rotational coordinates corresponds to a situation where the  $z$ -axis of the body-fixed frame and the  $z$ -axis of the space-fixed frame having its origin in the center of mass of the two nuclei coincide. In this case the derivation results in a constrained Hamiltonian having the form

$$\begin{aligned} \hat{H}^{\text{NR}}(r_{13}, r_{23}; r_{12}) &= -\frac{1}{2} \left( \frac{1}{m_3} + \frac{1}{m_1 + m_2} \right) \left( \frac{\partial^2}{\partial r_{13}^2} + \frac{2}{r_{13}} \frac{\partial}{\partial r_{13}} \right) \\ &\quad - \frac{1}{2} \left( \frac{1}{m_3} + \frac{1}{m_1 + m_2} \right) \left( \frac{\partial^2}{\partial r_{23}^2} + \frac{2}{r_{23}} \frac{\partial}{\partial r_{23}} \right) \\ &\quad - \frac{1}{2} \left( \frac{1}{m_3} + \frac{1}{m_1 + m_2} \right) \frac{r_{13}^2 + r_{23}^2 - r_{12}^2}{r_{13} r_{23}} \frac{\partial^2}{\partial r_{13} \partial r_{23}} \\ &\quad + \hat{V}(r_{13}, r_{23}; r_{12}), \end{aligned} \quad (10)$$

where NR refers to the separation of the two rotational coordinates. This Hamiltonian differs from  $\hat{H}^{\text{BO}}$  only in the

factor containing the masses of the particles and  $\hat{H}^{\text{NR}}$  yields  $\hat{H}^{\text{BO}}$  if the masses  $m_1$  and  $m_2$  tend to infinity. It is also worth comparing this operator to the results given in Table I, as the Hamiltonian of Eq. (10) can be derived from  $\hat{H}^{\text{AJC}}$  by eliminating certain terms.

### B. A nonorthogonal basis

In order to perform variational computations with the Hamiltonians  $\hat{H}^{\text{BO}}$ ,  $\hat{H}^{\text{AJC}}$ , and  $\hat{H}^{\text{NR}}$ , a suitable basis is needed. Let us define a two-dimensional basis function  $\phi_{ij}(r_{13}, r_{23}) = \exp(-a_i r_{13} - b_j r_{23})$ , where  $a_i$  and  $b_j$  are real positive parameters. These variational parameters are chosen as  $a_i = \alpha \beta^i$  and  $b_j = \alpha \beta^j$ . This set of functions satisfies the cusp condition, hence one can obtain accurate energies and wave functions with a relatively small number of basis functions. These basis functions are not orthogonal; therefore, the related overlap matrix has to be computed. This basis is a direct product of two one-dimensional basis sets, but the matrix representation of the Hamiltonian is not that of a direct-product matrix due to the coupled integration limits (triangle condition). The integrals

$$\int_0^{+\infty} \int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} r_{13} r_{23} \phi_{ij}(r_{13}, r_{23}) \hat{H} \phi_{kl}(r_{13}, r_{23}) dr_{13} dr_{23} \quad (11)$$

generate the desired Hamiltonian matrix elements.

### C. Hamiltonian matrix elements

Due to the choice of nonorthogonal basis functions, it is  $\mathbf{S}^{-1/2} \mathbf{H} \mathbf{S}^{-1/2}$  that needs to be diagonalized in order to solve the eigenproblem of the Hamiltonian. The computation of the overlap matrix  $\mathbf{S}$  is relatively simple and utilizes analytical forms. The coupled integration limits make the integral evaluation somewhat difficult, but within the framework of the BO approximation the kinetic energy matrix can be computed analytically. The BO Hamiltonian matrix becomes

$$\mathbf{H}^{\text{BO}} = \mathbf{T}^{\text{BO}} + \mathbf{V}, \quad (12)$$

where  $\mathbf{T}^{\text{BO}}$  is the matrix representation of  $\hat{T}^{\text{BO}}$  given in Eq. (4) and  $\mathbf{V}$  [Eq. (3) with fixed  $r_{12}$ ] is the matrix representation of the Coulomb potential, which is the same for the BO and the finite mass cases and can be set up analytically. If proper

finite masses are present in the Hamiltonian, the resulting matrix is

$$\mathbf{H}^{\text{AJC}} = \mathbf{T}^{\text{AJC}} + \mathbf{V}, \quad (13)$$

where  $\mathbf{T}^{\text{AJC}}$  is the matrix representation of the constrained  $J=0$  kinetic energy operator given in Table I. There are particular terms in  $\mathbf{T}^{\text{AJC}}$  which cannot be expressed by analytical formulae. For example, the gamma functions appear in the  $\mathbf{T}^{\text{AJC}}$  matrix elements. The numerical integrations can nevertheless be carried out with arbitrary precision employing computer algebra. In the present case the MATHEMATICA program package<sup>63</sup> was utilized for this purpose.

### D. The dissociation limit

It is desirable that an adiabatic molecular approximation yields the nearly exact atomic energies upon dissociation. This holds for the standard DBOC approximation, which yields atomic energies correct in first order for the symmetric isotopologues of H<sub>2</sub><sup>+</sup>.

To investigate the dissociation limit of H<sub>2</sub><sup>+</sup> and its isotopologues within the AJC approach, it is practical to choose another set of internal coordinates, this time involving two distances and an angle. Let  $r_{12}$  and  $r_{13}$  denote two interparticle distances. The third coordinate  $\chi$  is defined as the angle between the  $\mathbf{r}_{12}$  and  $\mathbf{r}_{13}$  interparticle vectors, which have their common origin on the first particle. The origin of the rotating frame corresponds to the first particle. The first and the second particles lie along the  $z'$  axis of the rotating frame, while the plane generated by the three masses has been chosen to be the  $x'z'$  plane. The orientation of the space-fixed versus the body-fixed frame is specified again by the three Euler angles. The volume element over these coordinates is  $r_{12}^2 r_{13}^2 \sin \chi \sin \theta dr_{12} dr_{13} d\chi d\theta d\psi$ . If the  $r_{12}$  coordinate is separated, while the nuclei are allowed to have proper finite masses, one can obtain the constrained Hamiltonian expressed in terms of the new internal coordinates. The dissociation problem of the isotopologues corresponds to the situation when the internuclear distance tends to infinity. Thus, the asymptotic form of the constrained Hamiltonian is

$$\hat{H}^\infty = \hat{H}^{(0)} + \hat{H}', \quad (14)$$

where

$$\hat{H}^{(0)} = -\frac{1}{2m_3} \left( \frac{\partial^2}{\partial r_{13}^2} + \frac{2}{r_{13}} \frac{\partial}{\partial r_{13}} + \frac{1}{r_{13}^2} \left( \frac{1}{\sin^2 \chi} \frac{\partial^2}{\partial \psi^2} + \frac{\partial^2}{\partial \chi^2} + \cot \chi \frac{\partial}{\partial \chi} \right) \right) - \frac{1}{r_{13}} \quad (15)$$

and

$$\begin{aligned} \hat{H}' = & -\frac{1}{2m_1} \left( \frac{\partial^2}{\partial r_{13}^2} + \frac{2}{r_{13}} \frac{\partial}{\partial r_{13}} + \frac{1}{r_{13}^2} \left( \frac{1}{\sin^2 \chi} \frac{\partial^2}{\partial \psi^2} + \frac{\partial^2}{\partial \chi^2} + \cot \chi \frac{\partial}{\partial \chi} \right) \right) - \frac{1}{2} \left( -\frac{m_2}{2m_1(m_1+m_2)} (1 + \cos 2\chi) \frac{\partial^2}{\partial r_{13}^2} \right. \\ & + \left( \frac{1}{m_1+m_2} - \frac{1}{m_1} \right) \frac{2}{r_{13}} \frac{\partial}{\partial r_{13}} \right) - \frac{1}{2} \left( \frac{m_2}{2m_1(m_1+m_2)r_{13}} (3 + \cos 2\chi) \frac{\partial}{\partial r_{13}} + \frac{m_2}{m_1(m_1+m_2)} \frac{\sin 2\chi}{r_{13}} \frac{\partial^2}{\partial r_{13} \partial \chi} \right) \\ & - \frac{1}{2} \left( \frac{m_2}{2m_1(m_1+m_2)r_{13}^2} (\cos 2\chi - 1) \frac{\partial^2}{\partial \chi^2} \right) - \frac{1}{2} \left( \frac{1}{m_1+m_2} - \frac{1}{m_1} + \frac{m_2}{m_1(m_1+m_2)} \cos 2\chi \right) \frac{\cot \chi}{r_{13}^2} \frac{\partial}{\partial \chi}. \end{aligned} \quad (16)$$

With the proposed partitioning of  $\hat{H}^\infty$ ,  $\hat{H}'$  can be regarded as a small perturbation. This partitioning is advantageous as the eigenproblem of  $\hat{H}^{(0)}$  (the BO Hamiltonian of the H atom) can be solved exactly. The ground-state eigenfunction of  $\hat{H}^{(0)}$  is given in atomic units as

$$\Psi^{(0)}(r_{13}, \chi, \psi) = \sqrt{\frac{m_3^3}{\pi}} \exp(-m_3 r_{13}), \quad (17)$$

while the corresponding ground-state energy is  $E^{(0)} = -m_3/2 E_h$ . Let the effect of  $\hat{H}'$  on the energy be taken into account in the first order of the Rayleigh–Schrödinger perturbation theory. Thus, to a very good approximation, the asymptotic AJC energy correction is

$$E^{(1)} = \int_0^{+\infty} dr_{13} \int_0^\pi d\chi \int_0^{2\pi} d\psi r_{13}^2 \sin \chi \Psi^{(0)}(r_{13}, \chi, \psi) \times \hat{H}' \Psi^{(0)}(r_{13}, \chi, \psi) = \frac{1}{6} \left( \frac{2}{m_1} + \frac{1}{m_1 + m_2} \right). \quad (18)$$

Note that due to our definition of the coordinate system,  $m_1$  is the mass of the nucleus holding the electron. In view of the complicated form of  $\hat{H}'$ , this expression is surprisingly simple and shows a very good agreement with the numerical results computed at large internuclear separations. One disturbing feature of this expression is that it contains the mass of the particle at infinite separation from the particle having the electron. The energy expression  $E^{(0)} + E^{(1)}$  shows that within the AJC approximation the energy of the separated particles will be different from the exact energies. For symmetrical isotopologues, ( $m_1 = m_2 = m$ ) and thus  $E^{(1)} = 5/(12m)$ , which equals 5/6 of the corresponding asymptotic DBOC correction.

### III. RESULTS AND DISCUSSION

Determination of the complete rotational-vibrational spectrum of the ground electronic state of the  $\text{H}_2^+$  molecular ion and its isotopologues provides challenges both for experiment and theory. The number of experimentally determined rovibrational energy levels is only 6(84) from the total of 481(637) levels corresponding to the ground electronic state of  $\text{H}_2^+(\text{HD}^+)$ .<sup>7,8</sup> Thus, it is clear that only theory is able to provide the complete set of rovibrational energy levels of  $\text{H}_2^+$ -like systems. Of course, for a simple system like this one can try to perform fully nonadiabatic computations that yield the rovibronic energy levels. Following the early works of Moss,<sup>7,8</sup> in 2000 Hilico *et al.*<sup>16</sup> computed the  $J=0$  and  $J=1$  states of  $\text{H}_2^+$  and its isotopologues employing a nonadiabatic nonrelativistic method. In 2006, Karr and Hilico<sup>13</sup> published the rotational-vibrational energy levels of the molecular ions  $\text{H}_2^+$ ,  $\text{D}_2^+$ , and  $\text{HD}^+$  up to  $J=2$ .

In this work we follow another strategy based on the adiabatic separation of the nuclear vibration from the other degrees of freedom. This adiabatic treatment results in a one-dimensional rovibrational Hamiltonian

$$\hat{H}^{\text{1D}} = -\frac{1}{2\mu_{12}} \frac{d^2}{dr_{12}^2} + \frac{J(J+1)}{2\mu_{12}r_{12}^2} + V_{\text{BO}}(r_{12}) + V_{\text{ad}}(r_{12}), \quad (19)$$

where  $V_{\text{BO}}$  is the BO potential and  $V_{\text{ad}}$  is the adiabatic correction, which can be either the traditional DBOC,  $V_{\text{DBOC}}$ , or the AJC,  $V_{\text{AJC}}$ , proposed in Part 1 of this study. The mass dependent constant is defined as  $\mu_{12} = m_1 m_2 / (m_1 + m_2)$ . The Schrödinger equation corresponding to  $\hat{H}^{\text{1D}}$  can be solved variationally for each  $J$ , thus all the rovibrational levels corresponding to the given potential energy curves can simply be computed.

The AJC energy corrections determined in Part 1 for isotopologues of the  $\text{H}_2^+$  system are not equivalent to the traditional diagonal BO energy corrections<sup>30,54–58</sup> used to correct clamped-nuclei electronic structure calculations. This is due to the different Hamiltonians used in the two formulations. Nevertheless, the AJCs allow a similar correction to the clamped-nuclei energies, thus maintaining the notion of a (mass-dependent) PES. Based on their definition, AJCs were expected to result in energy corrections closer to the ultimate nonadiabatic limit than the DBOC corrections. As established in Part 1 for the case of the isotopologues of  $\text{H}_2^+$ , at most internuclear distances the AJC correction is substantially smaller than the related DBOC correction. The actual AJC/DBOC ratio depends on the internuclear distance.

### A. Potential energy functions

The BO energies and the adiabatic corrections have been computed at 28 fixed values of the internuclear distance  $r_{12}$ . There are two electronic states of  $\text{H}_2^+$ , which have the same dissociation limit of  $-1/2 E_h$  within the BO approach. The ground electronic state (usually denoted as  $1s\sigma_g$  or  $X^2\Sigma_g^+$ ) has a minimum at around 2 bohr. The total BO energy at the equilibrium geometry is  $-0.602\ 634\ 62E_h$ . Thus, the corresponding equilibrium dissociation energy  $D_e$  is  $22\ 525.7\ \text{cm}^{-1}$ . The first excited electronic state (usually denoted as  $2p\sigma_u$  or  $A^2\Sigma_u^+$ ) is also bound with a minimum around 12.5 bohr. The  $D_e$  value corresponding to the BO potential of this essentially repulsive  $2p\sigma_u$  state is only  $13\ \text{cm}^{-1}$ .

For  $\text{H}_2^+$ ,  $\text{D}_2^+$ , and  $\text{HD}^+$  the ground-state ( $1s\sigma_g$ ) BO electronic energies, DBOCs, AJCs, as well as BO energies and AJCs for the  $2p\sigma_u$  state are given in Table II. The ground-state ( $1s\sigma_g$ ) DBOCs and AJCs for  $\text{H}_2^+$ ,  $\text{D}_2^+$ , and  $\text{HD}^+$  are given as a function of internuclear separation in Fig. 1.

The variational parameters of the basis functions were set to  $a_i = b_i = \alpha\beta^i$ , where  $i = -N, \dots, N$ . Thus, a two-dimensional basis of  $(2N+1)^2$  functions was defined. The two real positive parameters  $\alpha$  and  $\beta$  were optimized at each  $r_{12}$  internuclear distance.

The BO energies of  $\text{H}_2^+$  can be obtained with arbitrary precision by solving variationally the eigenvalue problem of Eq. (4). The lowest two eigenvalues of the matrix representation of Eq. (4) correspond to the BO electronic energies of

TABLE II. The ground-state ( $1s\sigma_g$ ) and the first excited state ( $2p\sigma_u$ ) BO total energies, DBOCs, and AJCs for H<sub>2</sub><sup>+</sup>, D<sub>2</sub><sup>+</sup>, and HD<sup>+</sup> as a function of the internuclear separation  $r_{12}$ . (The internuclear separations ( $r_{12}$ ) are given in bohrs. Complete basis set BO energies are in  $E_h$ , DBOCs computed at the HF/aug-cc-pv6Z level and the AJCs are given in cm<sup>-1</sup>. The nuclear masses employed for H and D are 1.007 276 47 and 2.013 553 21 u, respectively.)

$r_{12}$	$1s\sigma_g$							$2p\sigma_u$			
	BO <sup>a</sup>	H <sub>2</sub> <sup>+</sup> DBOC <sup>b</sup>	AJC <sup>c</sup>	D <sub>2</sub> <sup>+</sup> DBOC <sup>b</sup>	AJC <sup>c</sup>	HD <sup>+</sup> DBOC <sup>b</sup>	AJC <sup>c</sup>	BO <sup>a</sup>	H <sub>2</sub> <sup>+</sup> AJC <sup>c</sup>	D <sub>2</sub> <sup>+</sup> AJC <sup>c</sup>	HD <sup>+</sup> AJC <sup>c</sup>
1.00	-0.451 786 31	79.87	63.92	39.96	31.98	59.92	46.63	0.435 186 37	281.09	140.62	208.91
1.20	-0.528 974 52	73.00	57.97	36.52	29.00	54.76	42.36	0.244 730 65	211.86	105.99	156.88
1.40	-0.569 983 53	67.51	53.32	33.77	26.68	50.64	39.02	0.102 205 74	171.03	85.56	126.20
1.60	-0.590 937 23	63.12	49.67	31.58	24.85	47.35	36.40	-0.008 617 29	144.82	72.45	106.53
1.80	-0.600 253 63	59.63	46.80	29.83	23.42	44.73	34.34	-0.096 675 51	126.76	63.42	93.01
2.00	-0.602 634 21	56.87	44.54	28.45	22.29	42.66	32.71	-0.167 534 39	113.57	56.82	83.18
2.20	-0.600 839 63	54.71	42.78	27.37	21.40	41.04	31.44	-0.225 013 71	103.49	51.77	75.69
2.40	-0.596 553 64	53.05	41.42	26.54	20.72	39.79	30.46	-0.271 909 11	95.50	47.78	69.78
2.60	-0.590 833 20	51.80	40.40	25.91	20.21	38.86	29.73	-0.310 345 27	89.01	44.53	65.00
2.80	-0.584 356 00	50.90	39.66	25.46	19.84	38.18	29.20	-0.341 971 65	83.63	41.84	61.05
3.00	-0.577 562 86	50.30	39.17	25.16	19.60	37.73	28.84	-0.368 085 00	79.11	39.58	57.74
4.00	-0.546 084 88	50.37	39.26	25.20	19.64	37.79	28.91	-0.445 550 64	64.50	32.27	47.12
5.00	-0.524 420 30	52.96	41.67	26.49	20.85	39.72	30.65	-0.477 291 61	57.17	28.60	41.83
6.00	-0.511 969 05	55.66	44.48	27.84	22.26	41.75	32.67	-0.490 643 89	53.35	26.69	39.09
7.00	-0.505 594 00	57.55	46.68	28.79	23.36	43.17	34.23	-0.496 271 71	51.38	25.71	37.71
8.00	-0.502 570 39	58.63	48.06	29.33	24.05	43.98	35.17	-0.498 606 02	50.41	25.22	37.07
9.00	-0.501 195 45	59.20	48.84	29.61	24.44	44.41	35.57	-0.499 543 83	49.96	25.00	36.91
10.00	-0.500 578 73	59.48	49.25	29.76	24.64	44.62	35.48	-0.499 901 07	49.76	24.90	37.16
11.00	-0.500 299 23	59.62	49.47	29.83	24.75	44.72	34.71	-0.500 024 42	49.70	24.87	38.04
12.00	-0.500 168 31	59.69	49.58	29.86	24.81	44.77	32.82	-0.500 057 89	49.68	24.86	39.99
13.00	-0.500 103 50	59.72	49.65	29.88	24.84	44.80	30.20	-0.500 059 47	49.69	24.86	42.67
14.00	-0.500 068 95	59.74	49.68	29.88	24.86	44.81	28.23	-0.500 051 50	49.70	24.87	44.68
18.00	-0.500 021 96	59.76	49.75	29.89	24.89	44.83	26.59	-0.500 021 55	49.75	24.89	46.39
22.00	-0.500 009 70	59.76	49.77	29.90	24.90	44.83	26.56	-0.500 009 69	49.77	24.90	46.45
26.00	-0.500 004 95	59.76	49.78	29.90	24.91	44.83	26.57	-0.500 004 96	49.78	24.91	46.46
30.00	-0.500 002 79	59.76	49.78	29.90	24.91	44.83	26.57	-0.500 002 79	49.79	24.91	46.47

<sup>a</sup>Where available, the BO energies of the  $1s\sigma_g$  and  $2p\sigma_u$  states obtained in this study agree with those presented in Table I of Ref. 20 and Table I of Ref. 22.

<sup>b</sup>For up to  $r_{12}=10$  bohr, Bishop and Wetmore (Ref. 22) determined the DBOC corrections that agree with those presented here. Note that for  $r_{12}$  greater than 28 bohr, Schwenke (Ref. 30) obtained an appealing asymptotic form given there as Eq. (20).

<sup>c</sup>The AJCs are differences between the results obtained from calculations using proper finite and infinite nuclear masses. All the AJCs are converged within the given precision. The AJCs were computed with basis sets of (9 9) functions [denoted as ( $N_{23}$   $N_{13}$ ), where  $N_{23}$  and  $N_{13}$  are the number of  $r_{23}$ - and  $r_{13}$ -dependent basis functions, respectively].

the states  $1s\sigma_g$  and  $2p\sigma_u$ . The ground-state BO results were the same within the required precision as those obtained by Hartree–Fock limit (HFL) calculations based on distributed Gaussian basis functions.<sup>64</sup> The  $V_{\text{DBOC}}$  corrections corresponding to the electronic ground state were computed at the HF level employing the aug-cc-pV6Z basis.<sup>65</sup> The computations utilized the program package PSI3 (Ref. 66) and the formalism of Ref. 57. The AJC corrections were calculated as described in Sec. II and the results are converged to within 0.01 cm<sup>-1</sup>.

The potentials obtained were fitted in two steps. First, a modified Morse function with seven parameters was used for fitting in the region of 10–40 bohr. Second, the potential was fitted employing all the energy points from 1–40 bohr using the former Morse-type function with the preoptimized parameters and another modified Morse function with 15 parameters. The maximum and average errors of the fitting procedures were 0.07 and 0.02 cm<sup>-1</sup>, respectively.

The fitted curves have been applied during the solution of the one-dimensional (ro)vibrational Schrödinger equation

based on Eq. (19). Employing  $V_{\text{BO}}$ , one obtains the exact nonrelativistic (ro)vibrational energy levels within the BO approximation. One can go beyond the BO approximation by employing either the  $V_{\text{BO}}+V_{\text{DBOC}}$  or the  $V_{\text{BO}}+V_{\text{AJC}}$  potential. The accuracy of the fitted BO, DBOC, and AJC potentials means that one can easily determine two salient features of these potentials: equilibrium internuclear distances and equilibrium dissociation energies.

The equilibrium BO internuclear distance is 1.997 20 bohr. For H<sub>2</sub><sup>+</sup> and D<sub>2</sub><sup>+</sup>, it is increased by 0.000 54 and 0.000 27 bohrs by the adiabatic DBOC correction, respectively. The corresponding AJC shifts are 0.000 42 and 0.000 22 bohrs, respectively. These small corrections are still an order of magnitude larger than the DBOC corrections found for the isotopologues of the much heavier water molecule.<sup>67</sup>

For H<sub>2</sub><sup>+</sup>, the equilibrium BO, DBOC, and AJC dissociation energies are 22 525.7, 22 528.6, and 22 530.9 cm<sup>-1</sup>. This means that the DBOC correction increases  $D_e$  by 2.9 cm<sup>-1</sup>. In contrast, the AJC correction increases  $D_e$  by a much more significant 5.2 cm<sup>-1</sup>. As mass scaling arguments

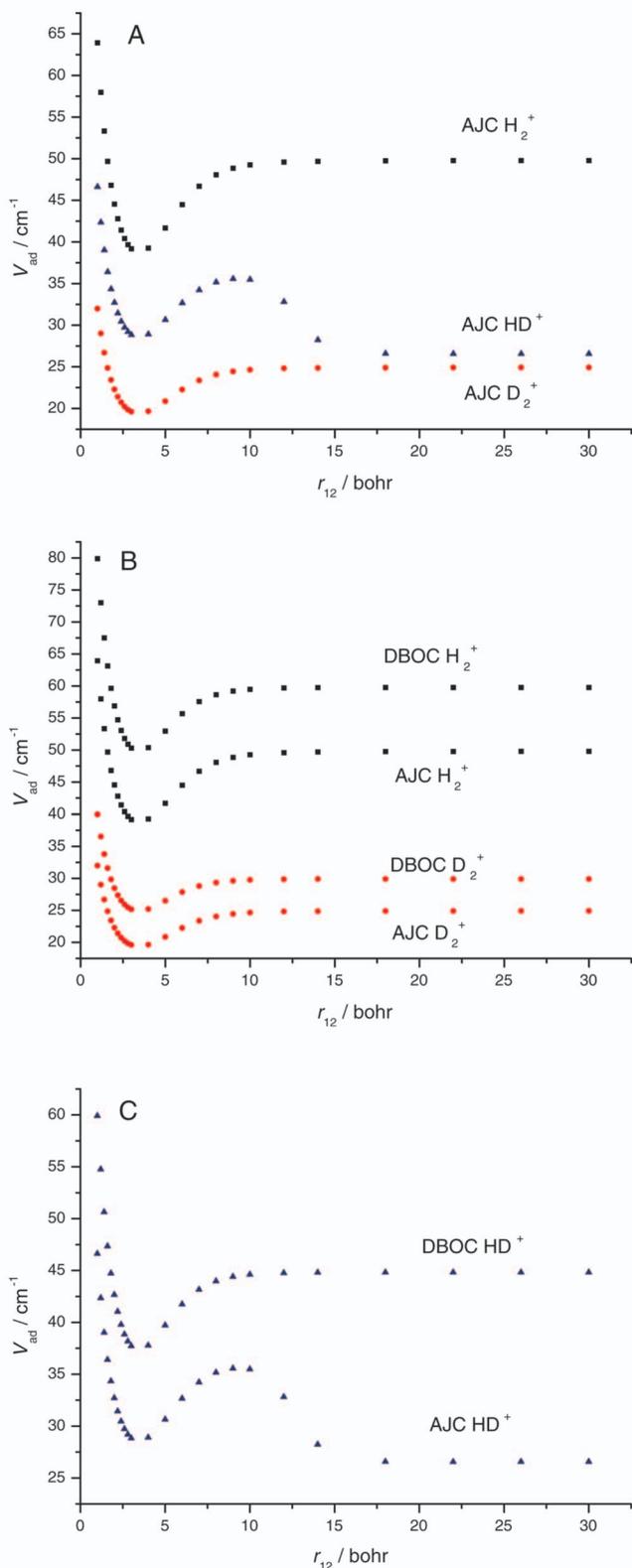


FIG. 1. (Color) Ground-state ( $1\sigma_g$ ) DBOCs and AJCs for  $\text{H}_2^+$ ,  $\text{D}_2^+$ , and  $\text{HD}^+$  as a function of internuclear separation. Panel (a) shows ground-state AJCs for  $\text{H}_2^+$ ,  $\text{D}_2^+$ , and  $\text{HD}^+$ , while ground-state DBOCs and AJCs are plotted on panel (b) for  $\text{H}_2^+$  and  $\text{D}_2^+$  and on panel (c) for  $\text{HD}^+$ , respectively.

would suggest, for  $\text{D}_2^+$  the DBOC and AJC increases are  $+1.45$  and  $+2.6$   $\text{cm}^{-1}$ , respectively. For  $\text{HD}^+$ , the DBOC and AJC corrections to  $D_e$  are  $+2.2$  and  $-6.1$   $\text{cm}^{-1}$ . The unexpected negative AJC result is again due to the lack of the  $g/u$

symmetry separation in the case of  $\text{HD}^+$  and the subsequent interaction and avoided crossing of the lowest two electronic states.

Finally, it is noted that the adiabatic DBOC and AJC corrections raise the potential curve relative to dissociation for  $r_{12} < 1.8$  bohr for  $\text{H}_2^+$  and  $\text{D}_2^+$ . For  $\text{HD}^+$ , the avoided crossing occurring in the vicinity of 10 bohr means that the AJC correction is larger at all internuclear separation than its asymptotic value.

## B. AJC versus DBOC energy corrections

The AJCs are smaller than the DBOCs for most internuclear distances and the difference between the DBOC and AJC corrections is not constant. At the united atom case, i.e., when the internuclear separation goes to zero, the AJC becomes the exact nonadiabatic energy correction of the united atom. The  $\hat{H}^{\text{NR}}$  Hamiltonian of Eq. (10) also provides the nonadiabatic results in the united atom limit. This approach yields smaller corrections than the AJC approach at all other geometries. (In what follows the results belonging to the ground electronic state are given in  $\text{cm}^{-1}$  and according to the order  $\{\text{H}_2^+, \text{D}_2^+, \text{HD}^+\}$ . For 1, 4, and 10 bohr internuclear separations, one gets  $\{58.13, 29.08, 38.77\}$ ,  $\{26.18, 13.10, 17.46\}$ , and  $\{29.67, 14.84, 19.79\}$  respectively.) In the united-atom limit the DBOC differs just slightly from the AJC. At the other extreme, at infinite separation, the DBOC goes almost to the correct atomic energy for the homoisotopologues, while the AJC energy is substantially different from the well-established atomic limit. This will be further investigated in Sec. III B 1.

The DBOC has the simple property that the DBOC values of the different isotopologues of  $\text{H}_2^+$  can be computed by scaling the DBOC of  $\text{H}_2^+$  (see, for example, Ref. 35). These mass-dependent scale factors are the same at each internuclear separation. Thus, the DBOC curves of  $\text{D}_2^+$  and  $\text{HD}^+$  can be obtained by multiplying the DBOCs of  $\text{H}_2^+$  with nuclear mass-dependent factors  $m_p/m_d=0.500\ 248$  and  $(1+m_p/m_d)/2=0.750\ 124$ , respectively, where  $m_p$  and  $m_d$  denote the masses of  $\text{H}^+$  and  $\text{D}^+$ , respectively. However, no obvious scale factor exists for the AJCs; therefore, it is useful to analyze our numerical AJC results.

All the AJCs of  $\text{D}_2^+$  given in Table II can be obtained within a precision of  $0.01$   $\text{cm}^{-1}$  by scaling the AJCs of  $\text{H}_2^+$  with a factor of 0.5003. This observation holds both for the  $1\sigma_g$  and  $2p\sigma_u$  states. However, in the case of  $\text{HD}^+$ , a factor independent of the internuclear separation does not exist, especially not between 10–18 bohr internuclear separations, where the lowest two states strongly interact and go through an avoided crossing. In the case of both the  $1\sigma_g$  and  $2p\sigma_u$  states a factor of 0.734 can be used to obtain the AJCs of  $\text{HD}^+$  if the internuclear separation is shorter than 10 bohr. In this case precision of the predicted AJCs is around  $0.1$   $\text{cm}^{-1}$ . Considering the  $1\sigma_g$  state between 10 and 18 bohr internuclear separations, the scale factor decreases from 0.72 to 0.53. However, the picture is opposite in the case of the  $2p\sigma_u$  state; the scale factor increases from 0.74 to 0.93 in the same nuclear distance interval.

### 1. The dissociation limit

The BO approach cannot distinguish between the different dissociation limits of the different isotopologues of H<sub>2</sub><sup>+</sup>. In particular, the BO approach gives the same dissociation energy limit even if the different electronic states, i.e.,  $1s\sigma_g$  or  $2p\sigma_u$ , of a nonsymmetric isotopologue, e.g., HD<sup>+</sup>, are considered. However, in reality the correct dissociation limit corresponds to the exact energy of the H or D atom in the case of H<sub>2</sub><sup>+</sup> and D<sub>2</sub><sup>+</sup>, respectively. The DBOCs of the symmetric isotopologues (with nuclear mass of  $m$ ) at the dissociation limit are the atomic DBOCs,  $1/(2m)$ , which differ only slightly from the exact nonadiabatic corrections,  $1/[2(m+1)]$ . The AJC limits are different from the DBOC ones; employing Eq. (18),  $5/(12m)$  can be given for the AJCs at the dissociation limit. In the case of H<sub>2</sub><sup>+</sup> and D<sub>2</sub><sup>+</sup> the dissociation limits of the states  $1s\sigma_g$  and  $2p\sigma_u$  are the same. While the exact and the DBOC values are very close (about 60 and 30 cm<sup>-1</sup> for H<sub>2</sub><sup>+</sup> and D<sub>2</sub><sup>+</sup>, respectively), the AJC energy corrections at about 50 and 25 cm<sup>-1</sup> are significantly different from these values.

The picture for the dissociation of the nonsymmetric isotopologues is quite different. First, let us consider the HD<sup>+</sup> molecular ion. HD<sup>+</sup> preferentially dissociates to H<sup>+</sup>+D and also to H+D<sup>+</sup>. The first dissociation channel corresponds to the  $1s\sigma_g$  state while the second channel belongs to the  $2p\sigma_u$  state. The energy difference between the two asymptotes is mere 29 cm<sup>-1</sup>, confirmed by the experiments.<sup>68</sup> Naturally, the BO approach cannot follow this symmetry breaking. Furthermore, the DBOC treatment is also unable to give a reasonable correction at the dissociation limit of HD<sup>+</sup> due to the fact that the DBOC correction at infinite internuclear separation is the average value of the atomic DBOCs. The AJC method can follow this charge asymmetry although the AJCs do not equal the exact nonadiabatic energies of the corresponding atoms. Considering the  $1s\sigma_g$  state, the AJC at the dissociation limit can be obtained employing Eq. (18), where  $m_1$  is  $m_d$  and  $m_2$  is  $m_p$ . For the higher dissociation channel,  $m_1$  is  $m_p$  and  $m_2$  is  $m_d$  in Eq. (18). By employing the  $\hat{H}^{\text{NR}}$  Hamiltonian of Eq. (10), the calculated corrections at a 30 bohr internuclear separation are 29.88 cm<sup>-1</sup> (H<sub>2</sub><sup>+</sup>), 14.95 cm<sup>-1</sup> (D<sub>2</sub><sup>+</sup>), and 19.93 cm<sup>-1</sup> (HD<sup>+</sup>). It is important to observe that the adiabatic corrections for the ground ( $1s\sigma_g$ ) and the first excited ( $2p\sigma_u$ ) states employing  $\hat{H}^{\text{NR}}$  become degenerate if the ion dissociates. This fact is not very surprising in the case of the symmetrical isotopologues but needs to be explained in the case of HD<sup>+</sup>. When considering Eq. (10) it is obvious that  $\hat{H}^{\text{NR}}$  is proportional to the clamped nuclei Hamiltonian [see Eq. (4)]. They only differ in a mass dependent factor. Thus  $\hat{H}^{\text{NR}}$  is unable to handle the asymmetry in the case of HD<sup>+</sup>.

AJCs at the dissociation limit of the ground electronic state, more precisely at a 30 bohr internuclear separation of the hypothetical systems ( $pp^*e$ ), have also been computed. The mass of  $p^*$  was varied between  $0.001m_p$  and  $1000m_p$ . The results are shown on Fig. 2. Excellent agreement can be seen between the computed values and the AJCs obtained by the use of the formula given in Eq. (18). As expected, at infinite internuclear separation the AJCs go to zero when one

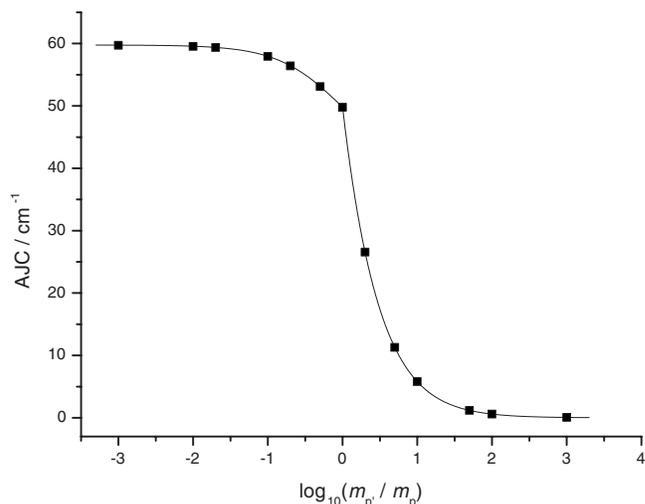


FIG. 2. AJCs of the ( $pp^*e$ ) systems at 30 bohr internuclear separation. The line drawn corresponds to Eq. (18).

of the nuclear masses is approaching infinity. If the mass of  $p^*$  becomes smaller and smaller, the AJC approaches the exact nonadiabatic energy of the H atom. It is important to note that Eq. (18) gives the DBOC of the H atom when the mass of  $p^*$  goes to zero, while the variationally computed AJC is the exact nonadiabatic correction.

Finally, we note that the AJCs can be computed by first-order perturbation theory employing the BO wave functions. The results obtained are shown in Fig. 3. The AJCs of the symmetric isotopologues of H<sub>2</sub><sup>+</sup> can be obtained within 0.1 cm<sup>-1</sup>. However, in the case of the nonsymmetric isotopologues, e.g., HD<sup>+</sup>, perturbation theory fails to work at long internuclear separations and, similarly to the DBOC, the perturbatively computed AJC of HD<sup>+</sup> is the average value of the AJC of H<sub>2</sub><sup>+</sup> and D<sub>2</sub><sup>+</sup> at the dissociation limit.

### C. Comparison with nonadiabatic results

In what follows, in case of the HD<sup>+</sup>, three possibilities will be considered allowing comparison with nonadiabatic

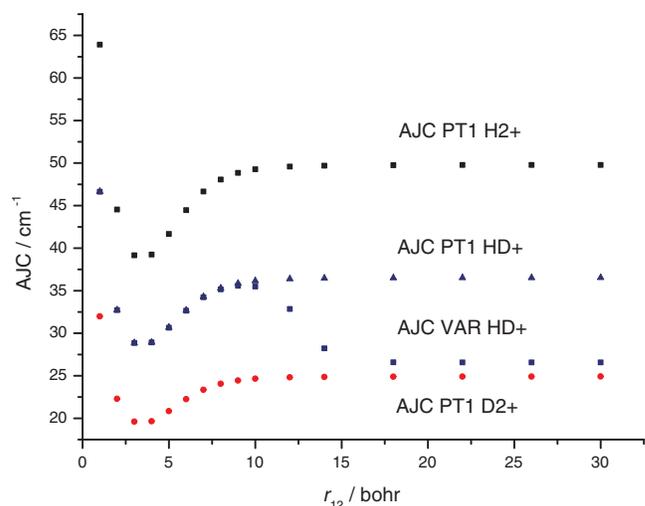


FIG. 3. (Color) First-order perturbatively computed ground-state ( $1s\sigma_g$ ) AJCs for H<sub>2</sub><sup>+</sup>, D<sub>2</sub><sup>+</sup>, and HD<sup>+</sup> as a function of internuclear separation. PT1 stands for first-order perturbation theory while VAR concerns the variational results.

results. First, average nuclear-electron distances are computed as a function of fixed internuclear separations employing the wave functions obtained by the AJC method. The average distances determined from the present approach can be compared to the nonadiabatic ones if the fixed internuclear distance in the adiabatic method is set to the expectation value of the  $d$ - $p$  distance corresponding to one of the vibrational states. Second, (ro)vibrational energy levels are computed by solving Eq. (19) and these (ro)vibrational states corresponding to an adiabatic potential are compared to the nonadiabatic levels. Third, the ground-state dissociation energies obtained by utilizing the  $V_{\text{BO}}$ ,  $V_{\text{BO}}+V_{\text{DBOC}}$ , and  $V_{\text{BO}}+V_{\text{AJC}}$  potentials are compared to nonadiabatic results.

### 1. Wave functions and expectation values

One-dimensional cuts of the electronic wave functions of the  $1s\sigma_g$  and  $2p\sigma_u$  states of  $\text{HD}^+$  are given in Figs. 4 and 5, respectively. These wave functions have been computed using the proper nuclear masses and fixing the internuclear separation at 2.055, 8.55, 12.95, and 28.62 bohr, distances corresponding to the average values of the  $p$ - $d$  distance at the  $v=0$ ,  $v=20$ ,  $v=21$ , and  $v=22$  vibrational states, respectively. These plots demonstrate that the AJC method is able to follow the symmetry breaking in  $\text{HD}^+$ , since considering the last two vibrational levels corresponding to the ground electronic state the asymmetry can clearly be seen in the wave functions. In the case of the  $1s\sigma_g$  state, the wave functions corresponding to long internuclear separations have a much higher peak at the position of  $d$  than around  $p$ . The picture is opposite in the case of the  $2p\sigma_u$  state since the electron density is much higher around the proton. Due to the proximity and the highly different character of the two states at large internuclear separations, their interaction, allowed by the broken nuclear symmetry present in the AJC approach, results in an unusual behavior.

Expectation values of the  $p$ - $e$  and  $d$ - $e$  distances were also computed using the AJC method. These results, given in Table III, can be compared to the nonadiabatic ones, since the full nonadiabatic problem of  $\text{HD}^+$  was solved variationally and expectation values of  $d$ - $p$ ,  $p$ - $e$ , and  $d$ - $e$  distances for the  $J=0$  vibrational levels of  $\text{HD}^+$  were computed by Bubin *et al.*<sup>32</sup> At short internuclear separations all the approaches, i.e., the BO, the AJC, and the nonadiabatic methods, provide the same average nuclear-electron distances. At long internuclear separations the BO approach fails to work, while the AJC method follows the symmetry breaking. Considering the last two vibrational states, i.e.,  $v=21$  and  $v=22$ , the nonadiabatic computation provided averaged  $p$ - $d$  values of 12.95 and 28.62 bohr and the nonadiabatic  $p$ - $e$ ( $d$ - $e$ ) averaged distances, all in bohr, were 12.19(2.306) and 28.55(1.600), respectively. Our adiabatic AJC method provides expectation values of 12.38(2.123) and 28.65(1.500) in order. Therefore, the pronounced asymmetry is recovered in the AJC results but the almost quantitative agreement between nonadiabatic and AJC results observed at short internuclear distances is not maintained at large separations when the  $2p\sigma_u$  state perturbs strongly the  $1s\sigma_g$  state. When using the  $\hat{H}^{\text{NR}}$  Hamiltonian given in Eq. (10), the computed  $p$ - $e$  and  $d$ - $e$  expecta-

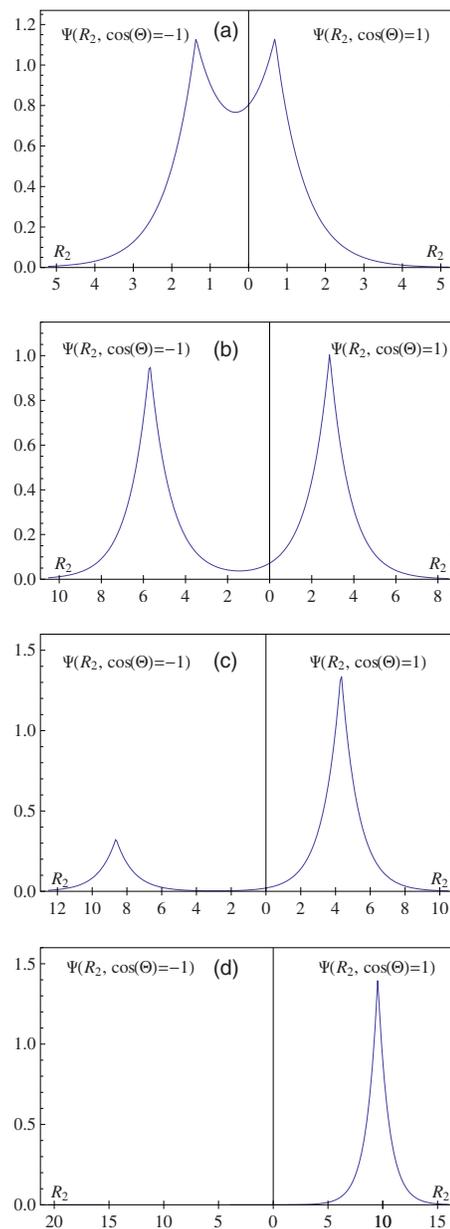


FIG. 4. (Color online) Wave functions  $\Psi(R_2, \cos \Theta = -1)$  and  $\Psi(R_2, \cos \Theta = 1)$  of  $\text{HD}^+$  corresponding to the state  $1s\sigma_g$ , where  $R_2$  is the distance of the electron from the center of mass of the two nuclei and  $\Theta$  is the angle between the internuclear vector and the electronic position vector, which has its origin at the center of mass of the two nuclei. The figures correspond to 2.055 (panel a), 8.55 (panel b), 12.95 (panel c), and 28.62 (panel d) bohr internuclear separations using proper finite masses for all three particles.

tion values remain the same for  $\text{HD}^+$  upon dissociation. As mentioned in connection with the dissociation limit, this Hamiltonian fails to exhibit the  $\text{HD}^+$  asymmetry, as it can be derived from the clamped nuclei Hamiltonian [Eq. (4)] by utilizing a simple mass-dependent scaling factor.

### 2. Vibrational energy levels and ground-state dissociation energies

All vibrational energy levels corresponding to the ground electronic state of  $\text{H}_2^+$ ,  $\text{D}_2^+$ , and  $\text{HD}^+$  computed in this study are given in Table IV. Detailed nonadiabatic nonrelativistic (and relativistic) energy values are available for these

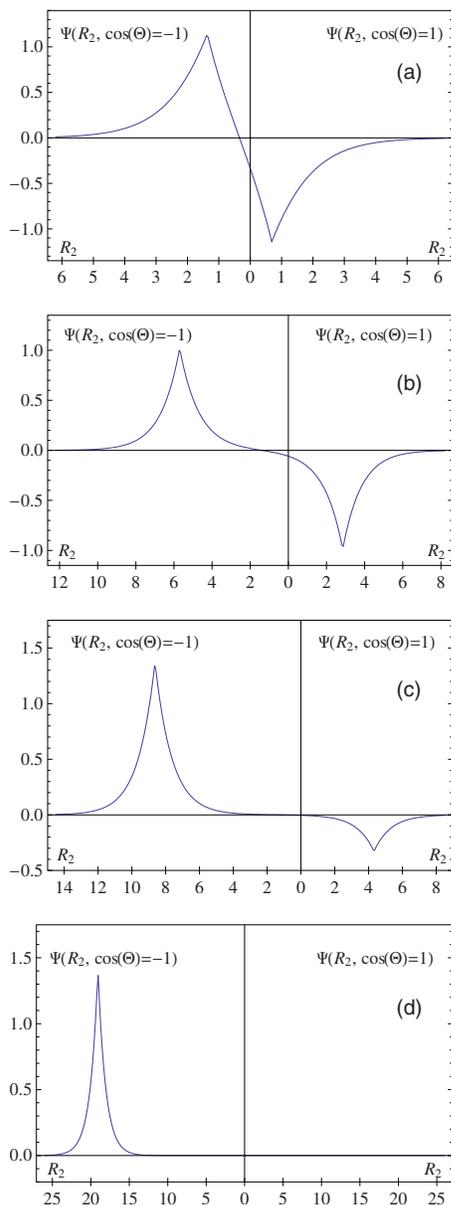


FIG. 5. (Color online) Wave functions  $\Psi(R_2, \cos \Theta = -1)$  and  $\Psi(R_2, \cos \Theta = 1)$  of  $\text{HD}^+$  corresponding to the state  $2p\sigma_u$ , where  $R_2$  is the distance of the electron from the center of mass of the two nuclei and  $\Theta$  is the angle between the internuclear vector and the electronic position vector, which has its origin at the center of mass of the two nuclei. The figures correspond to 2.055 (panel a), 8.55 (panel b), 12.95 (panel c), and 28.62 (panel d) bohr internuclear separations using proper finite masses for all three particles.

isotopologues from the literature. In this study, the nonrelativistic, nonadiabatic results serve as anchors for the discussion of the adiabatic vibrational energies.

The first observation is the excellent agreement between the BO and the nonadiabatic results, especially for the symmetrically substituted isotopologues for which a single potential curve well separated from all the other curves of the same symmetry exists. The BO errors are small for all the vibrational levels of  $\text{H}_2^+$ , starting only at  $0.4 \text{ cm}^{-1}$  for  $v=1$  and reaching  $2.9 \text{ cm}^{-1}$  for  $v=19$ . The discrepancies between the nonadiabatic and the BO levels change sign and magnitude in a somewhat uneven fashion. First they are negative and increase in magnitude (up to  $v=7$ ), then the corrections start decreasing, go through zero between  $v=13$  and  $14$ , and

end up at  $+2.9 \text{ cm}^{-1}$  for  $v=19$ . The picture is quite similar for  $\text{D}_2^+$ . Here the discrepancy reaches its largest negative value of  $-0.7 \text{ cm}^{-1}$  for  $v=10$  and  $11$ , goes through zero between  $v=19$  and  $20$ , and has its maximum positive value of  $+1.4 \text{ cm}^{-1}$  for the last level having  $v=27$ . The number of nonadiabatic and BO vibrational levels is the same for both isotopologues.

Due to the fact that the difference between the DBOC and AJC corrections is not constant, addition of either the DBOC or the AJC curve to the BO potential modifies the shape of the BO curve to a different extent. As a consequence, the two different adiabatic approaches result in different vibrational energy levels.

For the symmetric systems the DBOC corrections almost always help to lower the error of the BO approximation. For  $\text{H}_2^+$  and  $\text{D}_2^+$ , the nonadiabatic error, the deviation from the nonadiabatic results remaining after the adiabatic DBOC correction is applied to the BO potential, as a function of  $v$  is a simple curve with a single maximum. The nonadiabatic error is small for small  $v$ s, reaches its maximum value for about  $v=10$ , where it actually deviates more from the correct nonrelativistic nonadiabatic level than the BO level, and it is mere  $-0.1 \text{ cm}^{-1}$  for the penultimate levels and close to zero for the last levels. This means that for all the vibrational states of the symmetric isotopologues DBOC provides a valuable and accurate adiabatic correction.

As to the AJC potential, the nonadiabatic corrections remaining after the AJC corrections are applied to the BO curve grow monotonically up to the very last vibrational level. This is an important qualitative difference between the adiabatic DBOC and AJC corrections and makes the determination of an AJC correction factor easier than that for the DBOC curves. For all the levels of the symmetric isotopologues the AJC correction is worse than the DBOC correction.

The situation is quite different for  $\text{HD}^+$ . Here the BO approximation works very well again for all vibrational states whose  $d-p$  expectation value is less than the onset of interaction between the  $1s\sigma_g$  and  $2p\sigma_u$  states. This means  $v=1-20$ . The BO approximation “fails” for only the last two vibrational states, where the typical BO errors of less than  $1 \text{ cm}^{-1}$ , observed also for  $\text{H}_2^+$  and  $\text{D}_2^+$ , grow dramatically to  $5.9$  and  $12.4 \text{ cm}^{-1}$ , respectively. As to the nonadiabatic correction left after the consideration of the DBOC, the DBOCs again help for the lowest levels, up to  $v=8$  the DBOC errors are smaller than the BO ones, while between  $v=9$  and  $17$  the BO errors are smaller. The DBOC corrections help again for  $v=18$  and  $19$ . For the last three vibrational energy levels of  $\text{HD}^+$ , the error of the DBOC correction is larger than that of the BO. For the last state the BO error of  $-12.4 \text{ cm}^{-1}$  grows to  $-14.6 \text{ cm}^{-1}$  for the DBOC case. Furthermore, the DBOC corrections behave rather unevenly, their absolute values change through a maximum at  $v=12$ , and a minimum at  $v=19$ .

Just like for  $\text{H}_2^+$  and  $\text{D}_2^+$ , the nonadiabatic correction left after the AJC corrections has an almost monotonic behavior for  $\text{HD}^+$ . In absolute terms, AJC performs worse than BO for up to  $v=20$ . It is only for the last two states that AJC outperforms BO and DBOC. The use of the AJC correction is

TABLE III. Expectation values of the proton-electron distance  $r_{p-e}$  and the deuteron-electron distance  $r_{d-e}$  for the  $1s\sigma_g$  and  $2p\sigma_u$  electronic states of  $\text{HD}^+$ . All the distances are given in bohrs.

$r_{12}$	$1s\sigma_g$					$2p\sigma_u$		
	BO <sup>a</sup>		AJC method <sup>b</sup>		Nonadiabatic <sup>c</sup>	BO <sup>a</sup>		AJC method <sup>b</sup>
	$\langle r_{p-e} \rangle = \langle r_{d-e} \rangle$	$\langle r_{p-e} \rangle$	$\langle r_{d-e} \rangle$	$\langle r_{p-e} \rangle$	$\langle r_{d-e} \rangle$	$\langle r_{p-e} \rangle = \langle r_{d-e} \rangle$	$\langle r_{p-e} \rangle$	$\langle r_{d-e} \rangle$
1.000	1.138	1.138	1.138			2.218	2.219	2.219
2.000	1.659	1.659	1.659			2.134	2.134	2.134
2.055	1.688	1.688	1.688	1.688	1.688	2.143	2.144	2.144
4.000	2.717	2.719	2.716			2.850	2.851	2.219
6.227	3.875	3.887	3.863	3.910	3.821	3.909	3.897	3.921
7.099	4.319	4.349	4.290	4.421	4.198	4.338	4.309	4.367
8.550	5.051	5.181	4.922	5.516	4.569	5.057	4.928	5.187
10.00	5.777	6.341	5.215			5.779	5.217	6.343
12.95	7.251	12.38	2.123	12.19	2.306	7.251	2.123	12.38
28.62	15.07	28.65	1.500	28.55	1.600	15.07	1.500	28.65

<sup>a</sup>Expectation values are computed using the BO wave functions corresponding to fixed internuclear separations ( $r_{12}$ ).

<sup>b</sup>Expectation values corresponding to fixed internuclear separations ( $r_{12}$ ) are computed using the wave functions obtained from finite nuclear mass computations employing the constrained Hamiltonian given in Table I. The nuclear masses employed for H and D are 1.007 276 47 and 2.013 553 21 u, respectively. All the expectation values are converged within the given precision.

<sup>c</sup>Nonadiabatic results are taken from Ref. 32. In this case  $r_{12}$  is the averaged proton-deuteron distance corresponding to selected vibrational levels of  $\text{HD}^+$ .

clearly the best choice only for states close to the dissociation limit for the nonsymmetric isotopologues.

For  $\text{H}_2^+$  the ground-state BO, DBOC, and AJC dissociation energies are 21 376.2, 21 379.2, and 21 381.5  $\text{cm}^{-1}$ , respectively. The same results for  $\text{D}_2^+$  are 21 710.0, 21 711.5, and 21 712.7  $\text{cm}^{-1}$ , while for  $\text{HD}^+$  one obtains 21 528.7, 21 530.9, and 21 522.5  $\text{cm}^{-1}$ , respectively. The corresponding nonadiabatic results for  $\text{H}_2^+$ ,  $\text{D}_2^+$ , and  $\text{HD}^+$  are 21 379.3, 21 711.5, and 21 516.0, respectively.<sup>13</sup> Thus, for the symmetric isotopologues the DBOC approach outperforms the AJC approach. It basically recovers the full nonadiabatic correction, while for  $\text{HD}^+$  the error of the DBOC  $D_0$ , 14.9  $\text{cm}^{-1}$ , is more than twice that of the AJC  $D_0$ , 6.5  $\text{cm}^{-1}$ , and the adiabatic DBOC correction in this case even has the wrong sign.

The answer to the question whether adiabatic or nonadiabatic corrections to the BO energy levels are larger is somewhat unexpected although not without precedent.<sup>69</sup> Spectroscopic folklore suggests that nonadiabatic corrections are smaller than the adiabatic ones. Results of the present study for the extremely light  $\text{H}_2^+$  system certainly do not support this view. For  $\text{H}_2^+$  and  $\text{D}_2^+$  for all but the last few states the adiabatic correction is smaller, in the case of the AJC it is much smaller than the related nonadiabatic correction. The situation is similarly “counterintuitive” for  $\text{HD}^+$ . This means that for  $\text{H}_2^+$  and its isotopologues the adiabatic correction to the vibrational energy levels is smaller than the nonadiabatic correction for a large part of the spectrum. Although this result is strictly true only for the hydrogen molecular cation, it is expected to hold for other similar systems such as  $\text{H}_3^+$  and its isotopologues as well.

#### IV. CONCLUSIONS

It is generally accepted that (a) adiabatic corrections to the BO energies of rotational-vibrational levels are small for

electronically nondegenerate states, (b) the so-called nonadiabatic corrections are of the same order of magnitude as the adiabatic ones although they preferentially should be smaller, and (c) both corrections are largest for the lightest nuclei. Furthermore, in a recent study on the symmetric isotopologues  $\text{H}_2^+$  and  $\text{D}_2^+$ , Jaquet and Kutzelnigg<sup>37</sup> showed that nonadiabatic effects on vibration-rotation energy levels “have mainly to do with the participation of the electrons in the nuclear motion and hardly with the coupling of different electronic states.” Clearly,  $\text{H}_2^+$  and its isotopologues provide the simplest test cases where these beliefs can actually be probed.

Recently,<sup>35</sup> it appeared to us that a particularly appealing, physically motivated adiabatic separation leading directly to the concept of a mass-dependent potential energy curve incorporating the interaction of electronic states can be introduced for the three-body system of  $\text{H}_2^+$  and its isotopologues by separating only the internal motion of the two nuclei. Since this adiabatic approximation was introduced in Ref. 35 using the orthogonal Jacobi coordinates, the energy difference between this and the traditional BO approach was termed adiabatic correction (AJC).

In this study the correct form of the  $J=0$  constrained Hamiltonian corresponding to the AJC approximation was developed using the three interparticle distances as nonorthogonal coordinates. An asymptotic AJC energy correction formula was also developed, which, interestingly, contains the mass of the particle which is at infinite separation from the particle having the electron. Given the operators, efficient variational computations, based on a nonorthogonal basis of specially designed exponential functions, were performed yielding BO and AJC energies at a selection of internuclear distances for the  $\text{H}_2^+$ ,  $\text{D}_2^+$ , and  $\text{HD}^+$  systems. These energy value sets were augmented by DBOC corrections obtained using traditional electronic structure theory techniques. Next,

TABLE IV. The complete set of vibrational energy levels in cm<sup>-1</sup> corresponding to the electronic ground states of H<sub>2</sub><sup>+</sup>, D<sub>2</sub><sup>+</sup>, and HD<sup>+</sup> obtained from the nonrelativistic BO and the adiabatic DBOC and AJC approaches and compared to nonadiabatic (Nonad.) results.

<i>v</i> <sup>a</sup>	H <sub>2</sub> <sup>+</sup>				D <sub>2</sub> <sup>+</sup>				HD <sup>+</sup>			
	Nonad. <sup>b</sup>	BO <sup>c</sup>	DBOC <sup>d</sup>	AJC <sup>e</sup>	Nonad. <sup>b</sup>	BO <sup>c</sup>	DBOC <sup>d</sup>	AJC <sup>e</sup>	Nonad. <sup>b</sup>	BO <sup>c</sup>	DBOC <sup>d</sup>	AJC <sup>e</sup>
1	2191.10	-0.36	-0.20	-0.33	1577.07	-0.13	-0.08	-0.12	1912.97	-0.21	-0.15	-0.26
2	4254.99	-0.67	-0.39	-0.64	3089.45	-0.25	-0.15	-0.23	3729.81	-0.41	-0.29	-0.49
3	6195.89	-0.91	-0.55	-0.90	4538.78	-0.36	-0.21	-0.34	5453.38	-0.57	-0.42	-0.70
4	8017.37	-1.10	-0.70	-1.12	5926.51	-0.45	-0.27	-0.43	7086.16	-0.70	-0.54	-0.87
5	9722.36	-1.23	-0.83	-1.31	7253.96	-0.52	-0.32	-0.52	8630.28	-0.79	-0.64	-1.03
6	11 313.13	-1.31	-0.94	-1.47	8522.26	-0.58	-0.36	-0.59	10 087.50	-0.86	-0.73	-1.16
7	12 791.35	-1.33	-1.05	-1.61	9732.39	-0.63	-0.40	-0.66	11 459.22	-0.90	-0.82	-1.29
8	14 158.02	-1.30	-1.14	-1.72	10 885.17	-0.66	-0.45	-0.72	12 746.50	-0.91	-0.90	-1.39
9	15 413.47	-1.20	-1.20	-1.81	11 981.26	-0.68	-0.49	-0.77	13 950.02	-0.90	-0.97	-1.48
10	16 557.32	-1.03	-1.23	-1.86	13 021.17	-0.69	-0.54	-0.82	15 070.08	-0.85	-1.02	-1.55
11	17 588.41	-0.79	-1.22	-1.89	14 005.23	-0.69	-0.58	-0.87	16 106.60	-0.76	-1.05	-1.59
12	18 504.75	-0.49	-1.19	-1.90	14 933.62	-0.67	-0.61	-0.91	17 059.07	-0.63	-1.06	-1.61
13	19 303.41	-0.13	-1.12	-1.92	15 806.33	-0.63	-0.63	-0.93	17 926.53	-0.47	-1.05	-1.61
14	19 980.40	0.29	-1.03	-1.94	16 623.18	-0.57	-0.64	-0.95	18 707.53	-0.27	-1.02	-1.61
15	20 530.53	0.78	-0.88	-1.95	17 383.78	-0.49	-0.64	-0.96	19 400.09	-0.06	-0.98	-1.61
16	20 947.38	1.38	-0.65	-1.96	18 087.55	-0.40	-0.63	-0.97	20 001.62	0.18	-0.93	-1.61
17	21 223.64	2.04	-0.37	-1.99	18 733.68	-0.28	-0.61	-0.97	20 508.87	0.45	-0.86	-1.60
18	21 355.24	2.65	-0.13	-2.14	19 321.14	-0.16	-0.60	-0.97	20 917.85	0.84	-0.76	-1.57
19	21 378.55	2.84	-0.10	-2.35	19 848.60	-0.03	-0.58	-0.99	21 223.89	1.02	-0.69	-1.60
20					20 314.49	0.12	-0.55	-1.00	21 421.93	0.82	-1.10	-1.79
21					20 716.90	0.28	-0.51	-1.01	21 505.79	-5.85	-7.95	-4.34
22					21 053.61	0.48	-0.43	-1.01	21 515.58	-12.40	-14.58	-6.57
23					21 322.11	0.71	-0.32	-1.01				
24					21 519.74	0.95	-0.21	-1.02				
25					21 644.48	1.13	-0.18	-1.09				
26					21 699.38	1.35	-0.07	-1.13				
27					21 710.51	1.43	-0.02	-1.16				

<sup>a</sup>For H<sub>2</sub><sup>+</sup>, the *v*=0 vibrational energy levels are 1149.46, 1149.36, and 1149.44 cm<sup>-1</sup> corresponding to the  $V_{BO}$ ,  $V_{BO}+V_{DBOC}$ , and  $V_{BO}+V_{AJC}$  potentials, respectively. For D<sub>2</sub><sup>+</sup> and HD<sup>+</sup>, the *v*=0 vibrational energy levels are 815.67, 815.64, 815.67 and 997.03, 996.99, 997.04 cm<sup>-1</sup>, respectively, given in the same order of the potentials. The energy levels in the table are given relative to the corresponding *v*=0 vibrational energy level.

<sup>b</sup>Nonadiabatic results are taken from Ref. 13. Note that some of the energy levels for HD<sup>+</sup> have been confirmed and obtained with ultrahigh precision in Ref. 5.

<sup>c</sup>Differences between the nonadiabatic vibrational energies and those corresponding to the  $V_{BO}$  potential.  $m(H)=1.007\ 825\ 04$  u and  $m(D)=2.014\ 101\ 78$  u atomic masses were employed during the vibrational calculation.

<sup>d</sup>Differences between the nonadiabatic vibrational energies and those corresponding to the  $V_{BO}+V_{DBOC}$  potential.  $m(H)=1.007\ 276\ 47$  u and  $m(D)=2.013\ 553\ 21$  u nuclear masses were employed during the vibrational calculation. Moss determined a similar set of nonadiabatic corrections for H<sub>2</sub><sup>+</sup> given in the second column of Table IV in Ref. 10. They are slightly different on the order of 0.1 cm<sup>-1</sup> from those presented here.

<sup>e</sup>Differences between the nonadiabatic results and vibrational energies corresponding to the  $V_{BO}+V_{AJC}$  potential.  $m(H)=1.007\ 276\ 47$  u and  $m(D)=2.013\ 553\ 21$  u nuclear masses were employed during the vibrational calculation.

accurate potential energy functions have been developed for all three isotopologues and all three adiabatic cases (BO, DBOC, and AJC) by using modified Morse functions. These PESs facilitated the variational determination of all the vibrational energy levels of the systems H<sub>2</sub><sup>+</sup>, D<sub>2</sub><sup>+</sup>, and HD<sup>+</sup>.

The conclusions that can be drawn from all these computations can be summarized as follows.

The accurate PESs of this study allowed the determination of equilibrium internuclear distances and dissociation energies for the three isotopologues H<sub>2</sub><sup>+</sup>, D<sub>2</sub><sup>+</sup>, and HD<sup>+</sup>. The equilibrium BO distance is 1.997 20 bohr. For H<sub>2</sub><sup>+</sup> and D<sub>2</sub><sup>+</sup>, it is increased by 0.000 54 and 0.000 27 bohrs by the adiabatic DBOC correction, respectively. The corresponding AJC shifts are 0.000 42 and 0.000 22 bohrs, respectively. These small corrections are still an order of magnitude larger than the DBOC corrections found for the isotopologues of the

much heavier water molecule.<sup>67</sup> For H<sub>2</sub><sup>+</sup>, the equilibrium BO, DBOC, and AJC dissociation energies are 22 525.7, 22 528.6, and 22 530.9 cm<sup>-1</sup>. This means that the DBOC increases the BO  $D_e$  by 2.9 cm<sup>-1</sup>. In contrast, the AJC increases  $D_e$  by a much more significant 5.2 cm<sup>-1</sup>. As mass scaling arguments would suggest, for D<sub>2</sub><sup>+</sup> the DBOC and AJC increases are +1.45 and +2.6 cm<sup>-1</sup>, respectively. For HD<sup>+</sup>, the DBOC and AJC corrections to the BO  $D_e$  are +2.2 and -6.1 cm<sup>-1</sup>. Perhaps the unexpected negative AJC result is again due to the lack of the *g/u* symmetry separation in the case of HD<sup>+</sup> and the subsequent interaction and avoided crossing of the lowest two electronic states.

The AJC energy corrections are systematically smaller than the DBOC ones and the AJC/DBOC ratio depends on the internuclear distance. In the united-atom limit the AJC differs just slightly from the DBOC. At infinite separation,

the DBOC goes almost to the correct atomic energy for homoisotopologues, while the AJC energy is different from the well-established atomic limit.

The BO approach, relying on infinite nuclear masses, cannot distinguish between the different dissociation limits of the different isotopologues of  $H_2^+$ . For example, for  $HD^+$  the  $1s\sigma_g$  and  $2p\sigma_u$  electronic states have the same BO dissociation limits. The DBOCs of the symmetric isotopologues (with nuclear mass  $m$ ) at the dissociation limit are the atomic DBOCs,  $1/(2m)$ , which differ only slightly from the exact nonadiabatic value,  $1/[2(m+1)]$ . The AJC limit is  $\sim 5/(12m)$  and the AJC/DBOC ratio yields 5/6 to a good approximation. For  $HD^+$ , since the DBOC correction at infinite nuclear separation is the average value of the atomic DBOCs, the DBOC treatment is unable to give a reasonable correction at the dissociation limit. The AJC method can easily follow this charge asymmetry although the AJCs do not equal the exact nonadiabatic energies of the corresponding atoms.

In the case of  $HD^+$ , due to the proximity and the highly different character of the two lowest electronic states at large internuclear separations, their interaction, allowed by the broken nuclear symmetry present in the AJC approach, results in an unusual behavior. The pronounced asymmetry is recovered in the AJC results but the almost quantitative agreement between nonadiabatic and AJC results observed at short internuclear distances is not maintained at large separations when the  $2p\sigma_u$  state perturbs strongly the  $1s\sigma_g$  state.

There is an outstanding agreement between the BO and nonadiabatic energy levels for the well-separated lowest potentials of  $H_2^+$  and  $D_2^+$ . The discrepancies between the nonadiabatic and BO levels change sign and magnitude in a somewhat uneven fashion but never exceed 2.9 and 1.4  $cm^{-1}$  for  $H_2^+$  and  $D_2^+$ , respectively. For the symmetrical systems the adiabatic DBOC corrections almost always help lower the error of the BO approximation. For all the levels of the symmetric isotopologues the AJC correction is worse than the DBOC correction. Nevertheless, the nonadiabatic corrections remaining after the AJC corrections are applied to the BO curve grow monotonically up to the very last vibrational level; thus, determination of an AJC correction factor seems somewhat easier than that for the DBOC curves.

As to  $HD^+$ , the BO approximation works again very well for all vibrational states whose  $d$ - $p$  expectation value is less than the onset of interaction between the  $1s\sigma_g$  and  $2p\sigma_u$  states. The DBOC correction not only behaves unevenly (going through a maximum at  $v=12$  and a minimum at  $v=19$ ) but for the last three vibrational energy levels the error of the DBOC correction is larger than that of the BO. Unlike for the lower levels, for the last two states AJC outperforms both BO and DBOC. The use of the AJC correction is clearly the best choice only for states close to the dissociation limit for the nonsymmetric isotopologues.

Finally, note that for  $H_2^+$  and  $D_2^+$  for all but the last few vibrational states the adiabatic correction is smaller, in the case of the AJC it is much smaller than the related nonadiabatic correction. The situation is similarly counterintuitive for  $HD^+$ . This means that for  $H_2^+$  and its isotopologues the adiabatic correction to the vibrational energy levels is

smaller than the nonadiabatic correction for a large part of the spectrum. Although this result is strictly true only for the hydrogen molecular cation, it is expected to hold for other similar systems such as  $H_3^+$  and its isotopologues. It would be interesting to study further this behavior in other systems as well, for example, for the basically nonadiabatic muonic analogs of the  $H_2^+$  ion.<sup>70</sup> Overall, the present results support the above-mentioned assessment of Jaquet and Kutzelnigg<sup>37</sup> about the origin of nonadiabatic effects and suggest that by introducing coordinate-dependent masses in variational nuclear motion computations one can deal with a large part of the nonadiabatic effect.

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## APPENDIX: A CORRECTION OF PART 1

In Part 1<sup>35</sup> we investigated not only real but also counterfactual three-body systems. Thus, for example, we studied the effect of changes in (a) the value of the electron rest mass and (b) the mass of the unique particle (electron). In case (a) both  $m_p$  and  $m_e$  were changed while  $m_p/m_e$  remained 1836.15. Since minor inconsistencies slipped into Part 1, we recall here the relevant formulas and report the correct results and conclusions.

Let us consider counterfactual three-particle systems ( $ppe^*$ ) which contain two protons having either infinite or finite masses and one particle with unit negative charge having variable mass. In the case of infinite nuclear masses (a) and (b) provide, of course, the same results.

Considering the energies in cases (a) and (b), corresponding to infinite nuclear masses, the following exact formula holds [Eq. (32) in Part 1]:

$$E_{ppe^*}(R_1) = \frac{m_{e^*}}{m_e} E_{ppe} \left( \frac{m_{e^*}}{m_e} R_1 \right). \quad (A1)$$

Note that in contrast to the other parts of the present paper the internuclear distance is denoted here by  $R_1$  in order to follow the notation of Part 1. As to the AJCs, in case (b) the following *approximate* relation holds [Eq. (34) in Part 1]:

$$E_{ppe^*}^{AJC}(R_1) = \left( \frac{m_{e^*}}{m_e} \right)^2 E_{ppe}^{AJC} \left( \frac{m_{e^*}}{m_e} R_1 \right). \quad (A2)$$

As we showed in Part 1, Eq. (A2) is an excellent approximation if  $m_{e^*} \ll m_p$ . However, we stated incorrectly that in case (a) Eq. (A2) is an exact relation. Indeed, an exact formula holds for the AJC in case (a), which is

$$E_{ppe^*}^{AJC}(R_1) = \frac{m_{e^*}}{m_e} E_{ppe}^{AJC} \left( \frac{m_{e^*}}{m_e} R_1 \right). \quad (A3)$$

On the basis of the incorrect AJC formula for case (a), we wrote the following wrong conclusion in Part 1: "Since

the AJCs scale with the square of  $m_{e^*}/m_e$ , while the energies scale linearly, the decrease in the electron rest mass results in smaller and smaller AJCs in a relative sense. More importantly, the increase in either the electron rest mass or  $m_{e^*}$  means an increase in the breakdown of the BO approximation.” This statement should read correctly as follows: “Since in case (b) the AJCs scale with the square of  $m_{e^*}/m_e$ , while the energies scale linearly, the decrease in the electron mass provides relatively smaller and smaller AJCs. More importantly, the increase in  $m_{e^*}$  means an increase in the breakdown of the BO approximation. However, the increase in the electron rest mass *does not* mean an increase in the breakdown of the BO approximation if only Coulomb interaction is assumed between the particles, since in case (a) both the AJCs and the energies scale linearly.”

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